

On Demand Analysis: Glycols by HPLC/MS/MS

Case file notes for Dimock Residential Groundwater, WO 1201013, WO 1201015, WO 1202001, WO 1202003

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Samples were analyzed for diethylene glycol (DiG) (CAS# 111-46-6), triethylene glycol (TriG) (112-27-6), tetraethylene glycol (TeG) (112-60-7), 2-butoxyethanol (2-Bu) (111-76-2) and 2-methoxyethanol (109-86-4) by LC/MS/MS (inst id: TQD-LCMSMS) on a Waters Atlantis dC18 3um 2.1 x 150mm column (s/n- 0141301481). See the case file for complete instrument method information. Optima grade methanol and acetonitrile and 98-100% formic acid (bar codes: 5288, 11068, and 5278) were used. House deionized water was boiled before use. 2-Methoxyethanol was analyzed in a separate run from the other 4 target analytes.

An OASQA SOP for this method is in preparation. SOP R3QA239, Glycol Analysis by HPLC/MS/MS, is based on ASTM D 7731-11 and EPA SW-846 Methods 8000C and 8321 were followed for method development and QA/QC limits, where applicable. All applicable OASQA On Demand QA/QC protocols were followed.

The aqueous samples were injected without extraction onto the LC/MS/MS system. An appropriate surrogate has not been identified.

QC notes:

The method is under development, therefore, applicable QC limits for percent recoveries and RPDs are unknown. The default limits listed in SW-846 Method 8000C (80-120% for BS, CCV and SCV and 70-130% for matrix spikes and RPD of 25) were used. Values will be evaluated with future results to develop appropriate QC criteria.

Integration information:

In the Empower data report, manual integrations are indicated by lower case letters in the "int type" column. Baseline integration is indicated by a "b" and valleys are indicated by a "v". Upper case letters indicate processing according to the processing method parameters. The OASQA manual integration checklist is included in the case file when manual integrations were performed.

MS tuning and calibration:

Exact mass calibration is done annually with the preventive maintenance procedures. Mass calibration was successfully performed according to manufacturer's direction with NaCsI on 9/9/2011. The mass calibration summary report is included in the case file.

The system was tuned with authentic individual standards of each compound according to manufacturer's directions using the Waters Empower "Intellistart" tune/method development program in the MRM (multiple reaction monitoring) ESI+ (electrospray positive) mode. Tune data are included in the case file. Target masses, transitions and voltages determined in each compound's tune were compiled into appropriate instrument method sets. Only one MS tune file (which determines gas flow rates and source and

desolvation temperatures) may be used during a sample set run. For these analytes, the “tetraethylene glycol” tune was used for 2-Bu, DiG, TriG and TeG as it provided the best response for those targets. A separate run for 2-Me used the parameters defined by the “2 methoxy comb test” tune.

A second MRM mass transition was monitored for confirmation of each target where possible. Only one MRM was used for 2-Me. The response of the confirmation MRM was generally much lower than that of the primary MRM. While calibration curves were generated as part of the data processing and concentrations were calculated, the confirmations MRMs had much higher quantitation limits and less robust correlations than the primary MRM and were not used for reporting concentration, only for verification where possible. Method 8000C 11.10.4 recommends that if the concentration calculated for the confirmation MRM exhibits a +/- 40% relative percent difference from the primary MRM, the concentration should be considered estimated and the presence of the target suspect. The confirmation MRM is not applicable below 200ppb for the 3 glycols. The MRM confirmation for 2-Bu was calibrated to 10ppb.

Chromatographic method:

One instrument method set was used for 2-Bu, DiG, TriG and TeG and a separate method set was used for 2-Me. The mobile phase was comprised of water, acetonitrile and formic acid. See the instrument method reports for chromatographic conditions.

Initial and continuing calibration:

For 2-Bu, DiG, TriG and TeG:

Because the analytes exhibit variable responses, a wide range of initial calibration standard concentrations were prepared. Initial calibration standards from an UltraScientific custom standard mix of for 2-Bu, DiG, TriG and TeG were prepared at 500, 400, 300, 200, 100, 50, 25, 10 and 5ug/L (ppb). Where no response or known background interference for a target was evident, the concentration was removed from the processing method. Method 8000C cites a QC limit of $r^2 \geq 0.99$ for initial calibration curves. All primary MRMs met this criterion.

The second source calibration verification (SCV) standard was prepared from a custom mix supplied by AccuStandard. Comparison of the new SCV (std #1200011) used in this sample set to a previous SCV (#1100499) indicated that the concentration of 2-Bu was incorrect in standard #1200011. Comparison data run after the sample set is included in the case file. Standard 1100499 will be used in subsequent sample sets pending further information from the manufacturer.

Initial calibration standards for 2-Me were prepared from a neat standard from Accustandard. The second source verification was prepared from a neat standard from UltraScientific. A density of 0.966 kg/L as reported in the Merck Index (12th ed, 1996) was used to calculate concentrations.

Calibration ranges for both sets of analyses are as follows:

diethylene glycol:	25 - 500 ppb	(200-500ppb for the confirmation MRM)
triethylene glycol:	25 - 500 ppb	(200-500ppb for the confirmation MRM)

tetraethylene glycol: 25 - 500 ppb (200-500ppb for the confirmation MRM)
2-butoxyethanol: 5 - 500 ppb (10-500ppb for the confirmation MRM)
2-methoxyethanol: 10 - 500, no confirmation MRM

In some sample sets, 2-bu was only calibrated to 10ppb due to low response at 5ppb. NQLs were adjusted for affected samples in the Element report. In some sample sets, a high or low standard was eliminated from the IC curve due to low response or non-linearity. This is noted in the individual case file.

The Nominal Quantitation Limit (NQL)/Reporting Limit is the low standard concentration of the primary MRM.

See spreadsheet in the case file for continuing calibration (CCV) and SCV results. Outliers based on Method 8000C QC criteria have been flagged.

Because no extraction is performed with this method, CCV samples were also used as blank spike (BS) samples. According to OASQA On Demand procedures, a blank spike should be prepared at the NQL. Due to the varying NQLs, several low level BS's were analyzed in conjunction with mid-level CCV/BS samples. See the spreadsheet in the case file or chromatogram for results. Outliers are noted with each sample set. Mid-level BS results are reported in the Element reports. Some low level BS/CCV recoveries were outside Method 8000C's suggested limits. QC criteria have not been established for low level BS/CCVs. Some recent EPA methods, such as SW-846 Method 6850 (Perchlorate by HPLC/MS/MS) cite a QC limit of +/- 50% of the true value for low level CCVs, with more stringent limits for mid-level CCV samples. Recoveries will be tracked to determine appropriate limits. Results were qualified according to the OASQA Lab Quality Manual.

Matrix Spikes:

The matrix spike for sample 1201013-03 was prepared incorrectly for this sample batch. The matrix spike was reprepared and reanalyzed in the next sample batch. The reprepared results are reported in Element. Results for both preparations are included in the case file.

Method and instrument blanks:

Instrument blank (LCB, also referred to as IBL in the Region 3 OASQA Laboratory Quality Manual) and Method Blank (BLK) samples were analyzed concurrently since there was no extraction and both consisted of DI H₂O.

Results:

Only target analyte peak information is reported on chromatograms.